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VANADIUM EFFLORESCENCE
and its control by the
USE OF FLUORSPAR

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By

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ABSTRACT

The effect of fluorspar on the water-soluble vanadium content of four fired buff-burning clays was studied. Fluorspar was found to inhibit the development of water-soluble vanadium compounds to a greater or lesser extent in all of the clays. The inhibitory effect was much more pronounced in the less refractory clays that contained considerable illite. The kaolinitic clays required more fluorspar and higher firing temperatures to prevent the development of water-soluble compounds of vanadium.

INTRODUCTION

The appearance of yellow, green, or brown stain on buff brick has been the subject of study and discussion by a number of authors, including Hammer (1953), Lovejoy (1934), Curry (1926), Palmer (1929), Bosazza (1940), Kallauner and Hruda (1922), Seger (*in* Hecht and Cramer, 1902) and others. From their writings one may conclude that vanadium is the principal contributor to colored stain on buff brick, and that molybdenum, iron, chromium and nickel make secondary contributions. Alkali and alkaline earth metals are also usually present in the colored stains, but are not believed to contribute directly to the color. Study of the literature leads one to the tentative conclusion that the salts which cause colored efflorescence contain principally vanadium (and a small amount of molybdenum) in the form of alkali and alkaline earth vanadates and that such salts are sensitive to pH. From alkaline solutions colorless salts crystallize out, but from acid solutions colored

salts ranging from yellow through green to brown crystallize out (Jahr and Jander, 1934; Britton and Robinson, 1930; Jander and Jahr, 1933).

Very small amounts of vanadium cause colored stains on brick. Kallauner and Hruda (1922) found that the addition of as little as 0.001 percent of potassium vanadate to a pure kaolin produced yellow discoloration on bricks made therefrom. Bertrand (1950) states the amount of vanadium in clays to be usually small (within the limits of 10 to 1000 parts per million). Thus, even the smaller amount may cause objectionable stain on light-colored brick.

It has been observed (Bosazza, 1940; Hecht and Cramer, 1902; Kallauner and Kokta, 1941) that the vanadium in raw clay is not in a water-soluble form, but that heating the raw clay to temperatures of about $1000°C$ converts at least a part of the vanadium to soluble vanadates. Palmer (1929) found that the addition of alkali carbonates to the clay increased the amount of vanadium efflorescence on the fired bricks. He and co-workers also found that if their test bricks were fired to

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temperatures above 1000°C, vanadium efflorescence did not appear. He believed that this effect was due to fusion of vanadium compounds with other materials in the brick.

The exact mode of occurrence of vanadium in clays is not known. Hathaway (1955), on the basis of x-ray studies of vanadium micas, recently concluded that the vanadium replaced some of the aluminum in octahedral positions in the clay-like lattice. In raw clays, such as are ordinarily used in brick manufacture, there are many impurities. Vanadium could conceivably be present as water-insoluble vanadium minerals (Fioletov, 1929), as replacement for other ions in the clay lattice, as solid solution (Leutwein, 1941) with other impurities, as occupying base-exchange positions on the clay particles, or, as suggested by Hammer (1955), as incompletely weathered fragments of primary minerals, colloidal particles, or possibly organic complexes.

The prevention of vanadium stain on buff brick has been the main object of most experimental studies that deal with such stain. The problem has usually been approached in laboratory studies by investigating the effects of addition of small amounts of various materials to the clay before forming it into bricks. A number of materials have been reported to be effective. Lead and barium salts and various fluorides have all been reported to have inhibitory effects. Calcium fluoride in the form of fluorspar is the most promising from the economic angle because it is a plentiful natural material and because it need not be of high purity. Fines that contain considerably less calcium fluoride than acid grade fluorspar are relatively inexpensive. The small amounts of silica and other minerals that such fines contain are inconsequential in the brick.

The object of the present investigation was to obtain information of a fundamental nature on the formation of vanadium-type stain on bricks and on the effect of additions of fluorspar to the clay on the formation of such stains.

CLAY SAMPLES AND MATERIALS

The four clay samples studied were from operating brick plant pits. Brick made from all four clays were known to have displayed colored efflorescence to some degree at times. The operators of these plants had all had trouble with "green stain" to a greater or lesser degree. The plant methods used for control of "green stain" included: a) firing to higher temperatures; b) selective mining of clay (one operator claimed to be able to recognize by its appearance clay which would give trouble; c) adding fluorspar.

Clay S from an underground mine was of Pennsylvanian age and is described as an underclay associated with No. 2 coal in north central Illinois.

Clay L, also of Pennsylvanian age, sometimes referred to as the Tradewater clay, comes from a large open pit also in north central Illinois.

Clay M came from an open pit in western Indiana. The bed was less than 10 feet thick. It underlay 10 to 20 feet of overburden and a thin seam of coal.

Clay W was taken from a newly opened pit a few miles from the clay M working and was also adjacent to a thin seam of coal.

Several relatively pure clay minerals were collected so that the effect of fluorspar on their fired properties might be studied. These included a pure, well crystallized Georgia kaolin, a rather impure and poorly crystallized kaolin from Anna, Illinois, and a sample of illite from Fithian, Illinois, which is reputedly of high purity except for some free hydrous iron oxide (goethite).

The fluorspar used was known as acid grade, that is, its calcium fluoride content was 98 percent. As received, it was light gray and like fine sand in texture. It was ball milled for two hours before use.

PLAN OF EXPERIMENT

The small amounts of vanadium compounds in clay and in brick make their direct study very difficult, if not impossible. This difficulty, of course, is common in studies involving trace elements in mineral materials. The broad plan of experiment was to follow the vanadium content in certain buff-burning clays that were subjected to heat treatment both with and without the addition of fluorspar. It was planned to do this mainly by determining the water-extractable vanadium in the fired samples. In addition, studies of the original test clays and of the fired products were made in the hope that such studies would throw light on any phenomena involving vanadium in even a secondary way.

EXPERIMENTAL PROCEDURES AND TECHNIQUES USED

VANADIUM ANALYSIS

Vanadium analyses were carried out by the well known colorimetric phosphotungstate method described by Sandell (1950) and others. The analysis was supplemented in a few instances by spectrochemical analysis. Blanks were always run parallel with the analysis. The transmission measurements were made at 400 millimicrons with a Coleman model 14 spectrophotometer. The results were recorded as parts vanadium per million parts of sample dried at 110° C. The reproducibility of the analytical results was about ±10 percent of the amount of vanadium found in the range covered by most of the extraction experiments (30 p.p.m. and less). Most analyses were made in duplicate and the average of the two reported.

SAMPLE PREPARATION

Clays S and M were samples that had been ground at the plant. Clays W and L were ground in the laboratory in such manner as to give particle-size distributions as similar as possible to those of the plant-ground materials. When fluorspar was added to the clays, the composition was dry-mixed for 30 minutes in a covered laboratory model Simpson mixer with the rolls set to minimize grinding action. In all compositions the tempering water was mixed in by hand until a uniform plastic mud was obtained. This mud was hand-formed in a steel mold into 1″ x 1″ x 6″ bars with 60° wedge tips at one end. The bars were dried thoroughly before they were fired.

The bars were fired in an electric furnace with natural circulation of air. The total firing time was 18 hours in all cases. The time required to reach maximum temperature was 8 to 10 hours, depending on the desired temperature. At the end of the firing period the power was shut off and the furnace allowed to cool for 48 hours; at

the end of this period the fired bars were removed and used for all subsequent tests.

The samples on which differential thermal analyses were to be run were prepared separately in 10-gram batches. For compositions that contained fluorspar, the clay and fluorspar were weighed accurately on an analytical balance and ground together in a mullite mortar. The material was mixed thoroughly with water to form a heavy paste, dried at 110°C, and reground to pass a 100-mesh sieve. The heating curve was run on this material.

The clay (Georgia kaolin, Anna kaolin, and illite) and fluorspar mixtures to be used for x-ray studies were prepared in small batches, as described above, for differential thermal analysis samples. Small amounts of each composition were fired in platinum crucibles on the same schedule described for test bars.

Extraction of Vanadium

The water-soluble vanadium in the fired samples was determined by first crushing the fired bars and then grinding for two hours in a ball mill; 100 grams of ground, fired clay was then subjected to extraction for eight hours in a Soxhlet extractor using 300 milliliters of water; at the end of the period the amount of vanadium in the extract was determined.

Water Absorption

The water absorption of the fired test bars was determined by ASTM method C20-46 (1955).

Particle Size Analysis of Raw Clays

A particle size analysis in the range 0.5 micron to 30 microns was made on each raw clay. This was done by dispersing the clay in water contained in a thermostated cylinder and withdrawing portions of suspension with a pipette at intervals in the usual manner. The portions withdrawn were evaporated to dryness and the weight of dry residue determined.

X-ray diffraction patterns of each dry residue were made.

Clay M contained more coarse material than the others. It was therefore wet-screened on 100-mesh and 200-mesh screens to determine the percentage minus 149-microns and minus 74-microns.

X-ray Studies

X-ray powder diffraction patterns were prepared for clays fired to various temperatures and containing various amounts of fluorspar.

For unfired clays, oriented slides were prepared by allowing dispersed clay to settle out on clean microscope slides which lay at the bottom of the dish that contained the dispersion. The water was then evaporated on a steam bath leaving a layer of oriented clay particles on the slide. Diffraction patterns were then made from these slides.

The diffraction patterns were the basis of estimates of the amounts and kinds of minerals present in all samples, fired or raw. The estimates were made on the basis of accumulated data and experience of the X-ray Division of the Illinois State Geological Survey.

The x-ray equipment used was a General Electric XRD-3 Recording Spectrometer.

Differential Thermal Analysis (D.T.A.)

A schematic sketch of the apparatus used to determine the heating curves is shown in figure 1. A two-hole nickel
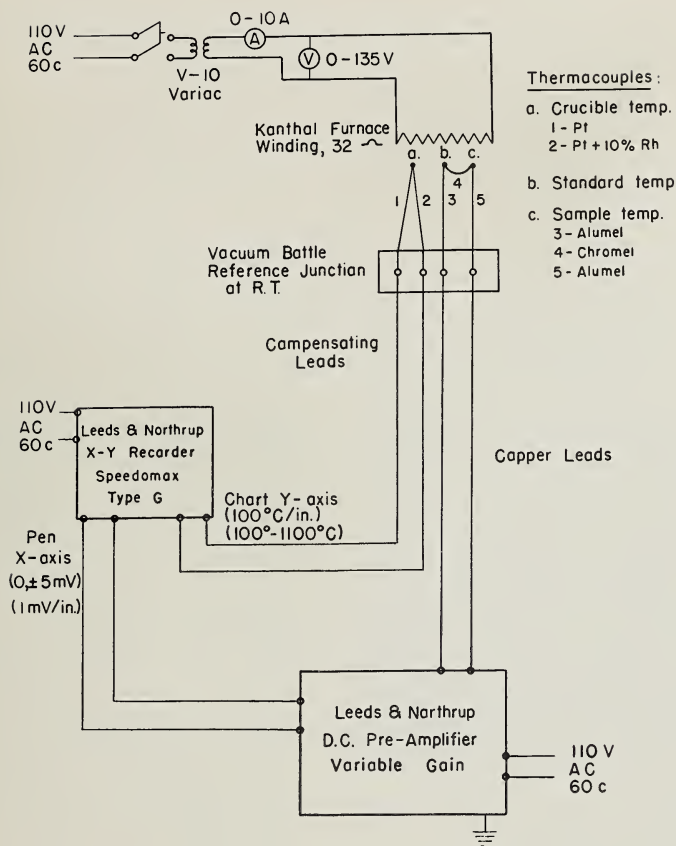
FIG. 1.—Schematic sketch of differential thermal
analysis apparatus.

block crucible was used. The sample was uniformly packed in one hole and calcined Al_2O_3 in the reference hole. The differential thermocouple was made of chromel-alumel wire and the crucible or furnace temperature thermocouple was platinum-platinum +10 percent rhodium. The furnace temperature thermocouple was inserted in a third hole in the nickel crucible midway between the sample and reference material holes. The heating rate was controlled by hand and it was easy, after some practice, to maintain the 10°C/minute temperature rise, used here, within the limits of 9.5° to 10.5° C/min. In some runs a block of nickel, lying loosely on top of the crucible, covered both holes of the crucible.

The pre-amplifier in the differential thermocouple circuit made it possible to easily change the sensitivity of the x-axis within wide limits. By changing the multiplier switch one could obtain sensitivities of 5.0μ volts/inch to 200μ volts/inch in six steps. In several runs the sensitivity was changed in the middle of the run to bring out details of thermal effects. The original diagrams were recorded on chart paper scale 100°C per inch with lines at every 10°C, making it possible to estimate the furnace temperature to a few degrees centigrade. The position of the

major peaks was estimated from the original diagrams. It will be noticed in later sections that all thermodiagrams start at 100°C. This is due to the fact that the recorder does not start to record until the furnace has reached this threshold temperature.

BASE EXCHANGE

A few very brief exploratory experiments were carried out to see if vanadium could be exchanged. Three 100-gram samples of each of the unfired clays were placed in 1000 ml. beakers and 500 ml. of 2N solutions of $AlCl_3$, $CaCl_2$ and $NH_4C_2H_3O_2$ were added. These were each stirred for 15 minutes with a mechanical stirrer and then placed on the steam bath for 24 hours. After digestion the clay was filtered off, using a Buchner vacuum funnel, and the filtrate concentrated to 100 ml. This concentrated filtrate was analyzed for vanadium by the spectrochemical method.

WICK TESTS

The wick test consisted of standing the fired bars on end in distilled water and recording the appearance of the material on the tapered tip after seven days. The 60° tapered tip served to concentrate the efflorescent salts and made the method quite sensitive. Some sam-

ples of the efflorescent material on the tips were studied to determine metals and ions present.

EXPERIMENTAL RESULTS

PROPERTIES AND COMPOSITION OF UNFIRED CLAYS

The results of the particle size analysis are given in table 1 and shown graphically in figure 2.
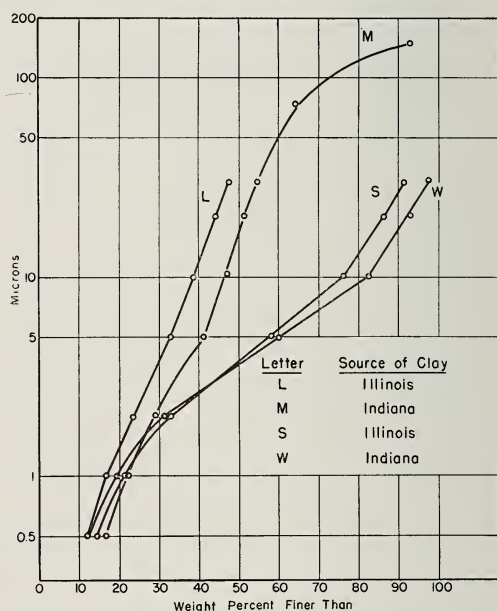
FIG. 2.—Particle size distribution of unfired clays.

From these results it appears that clays W and S are very fine, nearly 100 percent is less than 30 microns, whereas clays M and L are comparatively coarse, only 50 percent of the clay being less than 30 microns. However, the amount of very fine material (less than $\frac{1}{2}$ micron) is approximately the same for all clays.

The relative amounts of free quartz, illite, kaolinite, and montmorillonite+chlorite were estimated from the oriented slide type of x-ray pattern. It must be emphasized that these are only

TABLE 1.—PARTICLE SIZE ANALYSIS OF THE
UNFIRED CLAYS

Particle size (Microns)	Weight percent finer than			
	Clay W	Clay L	Clay S	Clay M
149	—	—	—	93.2
74	—	—	—	64.5
30	97.5	47.8	91.3	55.0
20	93.4	44.3	86.5	51.7
10	82.2	38.8	76.3	47.8
5	59.8	32.9	58.4	41.4
2	30.7	23.5	32.5	29.7
1	19.4	16.9	22.1	21.2
0.5	12.3	12.0	14.5	16.4

TABLE 2.—ESTIMATES OF QUARTZ AND CLAY MINERAL CONTENTS OF THE CLAYS

Particle size (Microns)	Clay S			Clay W			Clay M			
	Q*	I*	K*	Q	I	K	Q	I	K	M+C*
149	—	—	—	—	—	—	52	15	30	3
30	22	50	27	25	60	18	23	23	53	—
20	18	52	27	28	55	20	20	20	53	—
10	18	55	30	25	57	19	15	16	60	—
5	10	57	33	20	60	20	10	15	63	10
2	5	57	38	10	66	23	0	15	65	20
1	0	57	43	0	72	28	0	15	65	20

*Q=quartz; I=illite; K=kaolinite; M+C=montmorillonite and chlorite.

estimates and do not include other minor impurities such as pyrite, calcite, organic matter, etc. However, they are accurate enough to show up major differences between the clays. The results are shown in table 2. X-ray patterns of clay L were not made; therefore, its composition was not estimated.

Clays S and W contained no montmorillonite+chlorite and clay M contained only a small amount. The estimates for clays S and W, at 30-micron particle size, are taken to represent approximately the whole clay. However, for clay M the whole clay composition is probably represented fairly closely only at 149 microns. Thus the total clay mineral content of clays S and W is nearly 80 percent of the clay, but for clay M it is approximately 45 percent.

Clay M has twice the free quartz content of either S or W. A large portion of the quartz occurs as coarse material in whole clay M. In clays S and W the quartz content is much lower and its particle size is distributed over a lower range. So the difference between the particle size distribution curves of clays S and W compared to that of M is due predominately to differences in quartz grain size. The ratio of illite to kaolinite in the whole clay S is about two to one, in whole clay W it is three

to one, but in whole clay M it is 0.5 to one. This information is believed to be vital, as is shown below.

The vanadium content of the unfired whole clays and two fractions, one less than 2 microns and one more than 2 microns, were determined. Results of the analysis are shown in table 3.

Whole clays S and W have higher vanadium contents than M and L. This may be due to the fact that S and W have higher clay mineral contents. These data (table 3) indicate that the vanadium is more concentrated in the finer fractions of the whole clays.

TABLE 3.—VANADIUM CONTENT OF UNFIRED CLAYS
In parts per million

Clay Fraction	Clay S	Clay W	Clay M	Clay L
Whole clay	138	140	56	70
>2 microns	83	88	13	15
<2 microns	144	142	84	143

In order to determine the water extractability of vanadium in the unfired whole clays, samples of each dried clay were extracted for 8 hours in a Soxhlet continuous extractor. The results showed for clay L, 0.30 p.p.m. of vanadium in the extract; clay W, 0.80; clay M, 0.40; and clay S, 0.40.
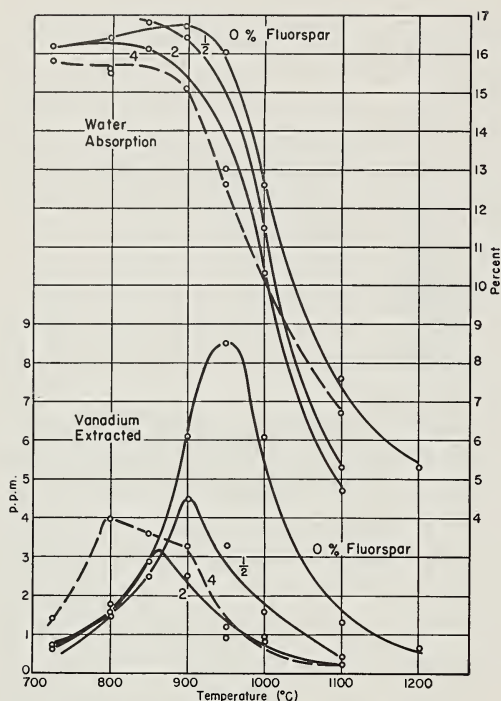
Fig. 3.—Effect of fluorspar content and firing temperature on vanadium extracted and on water absorption for clay S.

Fig. 4.—Effect of fluorspar content and firing temperature on vanadium extracted and on water absorption for clay M.

If the vanadium were associated with the clay minerals, it was thought that it might be in an exchangeable position. An attempt was made to exchange Al^{3+}, Ca^{2+}, and NH_4^+ cations. The results showed that no detectable amount of vanadium could be exchanged for the above ions in any of the clays.

Properties of Fired Clays

This section centers around the effect of temperature and fluorspar content on the extractability of vanadium from clays and an investigation of other properties which might directly or indirectly shed light on the mechanism of these two effects.

The effect of firing temperature and fluorspar content on the amount of vanadium extractable by the Soxhlet method and the water absorption of the fired clay bars are given in table 4.
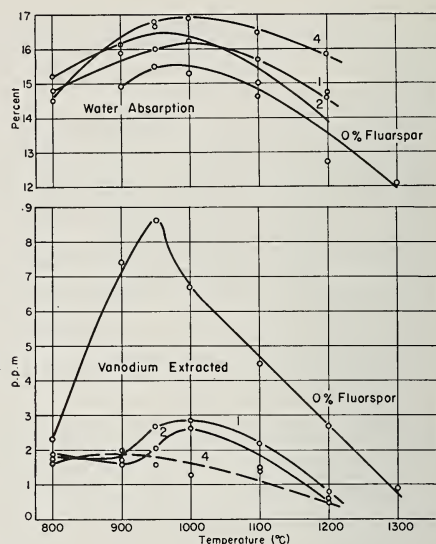
A portion of the data in table 4 for clays M and S are shown in figures 3 and 4. Several things stand out in these figures. First, the amount of vanadium extracted remains constant and small until the temperature reaches 650° to 700°C, then the amount of vanadium extracted rises rapidly with temperature to about 950°C, after which it drops. It will be noted that the drop in the amount of extracted vanadium with respect to rising temperature is much more rapid for clay S than for clay M. Second, the water absorption of both clays S and M reaches a maximum at about 950°C, but for clay S it drops much more rapidly with rising temperature than for clay M. It was noticed that clay S began to overfire between 1200° and 1300°C, whereas clay M showed no signs of overfiring at 1300°C. Clay W also showed signs of overfiring at 1200° to 1300°C.

TABLE 4.—EFFECT OF FIRING TEMPERATURE AND FLUORSPAR CONTENT ON VANADIUM EXTRACTABILITY
(BY SOXHLET METHOD) AND WATER ABSORPTION OF CLAYS S, M, L AND W
Top figure—vanadium p.p.m.
Bottom figure—water absorption, percent

Clay	Fluorspar content (percent)	Degrees C					
		100	650	725	800	850	900
S	0	0.40 —	0.12 16.1	— —	1.5 16.4	— —	6.1 16.7
S	½	— —	— —	0.70 17.0	1.6 16.5	2.5 16.8	4.5 16.4
S	1	— —	— —	0.92 16.5	1.9 15.9	3.1 16.6	3.2 16.7
S	2	— —	— —	0.65 16.2	1.8 15.6	2.9 16.1	2.5 16.6
S	4	— —	— —	1.4 15.8	4.0 15.5	3.6 16.4	3.3 15.1
M	0	0.40 —	0.55 13.6	— —	2.3 —	— —	7.4 14.9
M	½	— —	— —	— —	1.6 15.6	— —	2.1 15.6
M	1	— —	— —	— —	1.8 14.8	— —	1.7 14.9
M	2	— —	— —	— —	1.9 15.2	— —	1.6 16.1
M	4	— —	— —	— —	1.6 14.5	— —	2.0 15.9
L	0	0.30 —	0.45 14.1	— —	2.2 15.0	— —	5.2 14.7
W	0	0.80 —	0.12 19.3	— —	3.1 18.2	— —	8.5 18.1

Fluorspar, in general, reduces the amount of vanadium extracted from both clays S and M. The shape of the curves for clay S at one-half and two percent fluorspar shows that the extraction peak has been shifted back to lower temperatures, but for clay M the peak at one and two percent fluorspar has been slightly shifted to higher temperatures.

The amount of vanadium extracted compared to the amount of vanadium in the whole clay is rather small. It was suspected that possibly the Soxh-let method of extraction was not removing all the soluble vanadium. So to check the extraction efficiency of the Soxhlet method, clay S, fired at 900°C and containing zero to four percent fluorspar, was extracted in a continuous flow column extractor, which was thought to be more efficient. The procedure was to first extract by the usual Soxhlet method, then extract this same clay with several 500 cc charges of water in the column extractor. Each 500 cc through the column was analyzed for vanadium and the results are shown in table 5.

TABLE 4.—Continued

Clay	Fluorspar content (percent)	Degrees C				
		950	1000	1100	1200	1300
S	0	8.5 16.0	6.1 12.6	1.3 7.6	0.67 5.3	0.70 10.6
S	½	3.3 16.0	1.6 11.5	0.42 5.3	— —	— —
S	1	1.8 14.7	1.1 11.0	0.40 5.0	— —	— —
S	2	0.90 13.0	0.93 10.3	0.20 4.7	— —	— —
S	4	1.2 12.6	0.86 10.3	0.22 6.7	— —	— —
M	0	8.6 15.5	6.7 15.3	4.5 15.0	2.7 12.7	0.92 12.1
M	½	3.3 15.8	2.7 15.9	2.2 15.7	1.1 14.1	— —
M	1	2.7 16.0	2.9 16.2	2.2 15.7	0.85 14.6	— —
M	2	2.1 16.6	2.7 15.2	1.4 14.6	0.55 14.7	— —
M	4	1.6 16.9	1.3 17.0	1.3 16.5	0.50 15.9	— —
L	0	7.3 15.7	6.4 15.3	2.3 15.2	1.6 12.2	0.77 11.7
L	0	9.2 16.7	4.6 12.8	0.80 2.5	0.67 4.2	0.80 13.2

TABLE 5.—VANADIUM EXTRACTED (p.p.m.) BY THE SOXHLET METHOD AND THE COLUMN METHOD
Firing temperature 900°C

Clay	Fluorspar (percent)	Soxhlet After 8 hrs.	Column method			Total (both methods)
			After 1st 500 cc	After 2nd 500 cc	After 3rd 500 cc	
S	0	6.1	4.7	1.2	0.4	12.4
S	½	4.5	3.3	0.7	0.2	8.7
S	1	3.2	2.6	0.6	0.3	6.7
S	2	2.5	2.2	0.7	—	5.4
S	4	3.3	2.2	0.4	—	5.9

It looks as though eight hours of Soxhlet extraction removes about one-half the total amount of extractable vanadium removable by the combined methods. It also appears that the Soxhlet method is a relative test procedure and not an absolute method; however, it should be noted that the general trend of the vanadium extracted vs. the fluorspar content for the Soxhlet method is the same as the totals column in table 5.

TABLE 6.—TOTAL VANADIUM CONTENT OF CLAYS S, M, L, AND W FIRED TO VARIOUS TEMPERATURES
Vanadium in p.p.m.

Clay	Fluorspar (percent)	Degrees C				
		100	900	1000	1200	1300
S	0	138	—	144	122	100
S	½	—	—	146	—	—
S	1	—	—	129	—	—
S	2	—	146	135	—	—
S	4	—	132	142	—	—
M	0	56	56	56	54	44
M	½	—	52	43	—	—
M	1	—	43	50	—	—
M	2	—	35	50	—	—
M	4	—	45	—	—	—
L	0	70	—	72	66	38
W	0	140	—	141	143	108

The amount of vanadium extracted under the best conditions is small compared to the total amount present in the raw clay, indicating that the conversion of vanadium from the insoluble to the soluble form is incomplete.

Firing to high temperatures or the use of fluorspar appear to reduce the amount of vanadium extracted. It has been reported that vanadium is lost when mixtures of calcium fluoride and vanadium pentoxide are heated together (Prandtl and Mautz, 1911), a fact which suggests that fluorspar may control efflorescence by promoting elimination of vanadium by volatilization. To check this, clays S and M, fired to various temperatures and containing various amounts of fluorspar were analyzed for their vanadium content. The results are shown in table 6.

It appears that fluorspar does not cause any significant loss of vanadium, at least within the reliability of the data and at temperatures up to 1000°C in a clean oxidizing atmosphere. The data for all clays which contain no fluorspar indicate some loss of vanadium at temperatures of 1200° to 1300°C.

The bars of fired clay were allowed to stand for seven days in distilled water. At the end of this period the color of the tips of the bars was recorded as shown in table 7. No attempt was made to estimate the amounts of efflorescence except for clay M.

The dotted lines in table 7 show the approximate concentrations of fluorspar and firing temperatures required to eliminate the appearance of colored efflorescence on the wick test bars.

From the results of table 7 the bars containing no fluorspar show colored efflorescence in the vicinity of the extractability peak shown in table 4 and figures 3 and 4. On the low-temperature side of the peak, that is up to about 800°C, white efflorescence is formed, then colored efflorescence up to 950°C. On the high-temperature side of the extractability peak, colored efflorescence is present until the temperature is high enough to eliminate all efflorescence. In clay S fluorspar effectively eliminates the colored efflorescence at lower temperatures; however, it is not nearly as effective in clay M.

The efflorescence formed on the tip of the bars of clays S, L, and W was a

TABLE 7.—WICK TEST RESULTS AFTER SEVEN DAYS

N = No efflorescence
W = White efflorescence only
C = Colored efflorescence easily detected
♯ = Colored efflorescence detected only by close examination
Lines indicate approximate limits of colored efflorescence

Clay	Fluorspar (percent)	Degrees C									
		650	725	800	850	900	950	1000	1100	1200	1300
S	0	W	—	W	—	C	C	C	N	N	—
S	½	—	W	W	W	C	C	C	N	—	—
S	1	—	W	W	W	C	C	N	N	—	—
S	2	—	W	W	W	N	N	N	N	—	—
S	4	—	W	W	W	N	N	N	N	—	—
M	0	W	—	W	—	C	C	C	C	C	N
M	½	—	—	W	—	C	C	C	C	C	—
M	1	—	—	W	—	C	C	C	C♯	C♯	—
M	2	—	—	W	—	C	C	C	C♯	N	—
M	4	—	—	W	—	C	C	C♯	C♯	N	—
L	0	W	—	C	—	C	C	C	C	N	N
W	0	W	—	W	—	C	C	C	N	N	N

yellow-orange color but that on bars of clay M showed much more green. The efflorescent material on the tip of bars made from clays S, L, M and W containing no fluorspar and fired to 950°C and 1000°C was examined spectrochemically. The results are given in table 8. The numbers indicate only relative abundances and are not to be taken as representing composition in any units. Microchemical tests showed that a considerable amount of sulfate was present in this efflorescent material.

These results show that vanadium is rather abundant in the efflorescence formed on clays S and W and is fairly abundant in that formed on clays L and M. Molybdenum occurs in the efflorescence on all the clays, but is not as abundant as vanadium. It is probably a fair guess to say that vanadium compounds with Na, K, and Ca, are the main sources of the color in the efflorescent material. Colored molybdates are possibly contributing some color, as indicated by Palmer (1929).

Fluorspar in amounts larger than 2 percent darkens the fired color of both clays S and M at temperatures above 900° to 1000°C.

An x-ray examination of clays S and M was carried out. Table 9 summarizes the crystalline phases identified in each sample.

The quartz and anatase are impurities in the raw clay, but the rutile and hematite are formed from impurities when the clay is fired. The illite (as the anhydrous modification) (Grim and

TABLE 8.—SPECTROCHEMICAL ESTIMATE OF THE RELATIVE ABUNDANCE OF METALS IN COLORED EFFLORESCENCE

No fluorspar

Metal	Clay			
	L	M	S	W
Fired to 950°				
V	14	18	38	47
Na	7	4	39	24
K	15	18	19	24
Ca	59	56	Tr.*	Tr.
Mg	4	4	4	5
Mo	2	6	16	14
Cr	Tr.	Tr.	Tr.	Tr.
Sr	Tr.	Tr.	Tr.	Tr.
Fe	Tr.	N. D.*	N. D.	N. D.
Li	N. D.	Tr.	Tr.	Tr.
Fired to 1000° C				
V	10	15	27	44
Na	6	5	8	13
K	32	37	38	37
Ca	47	37	25	5
Mg	4	6	2	1
Mo	0.5	6	8	5

*Tr. = trace; N.D. = not detected.

Bradley, 1940) in clays S and M decreases in amount until it disappears between 850° and 950°C. In clay S, which contains more illite than clay M, some spinel is formed at 800°C and is still detectable at 1000°C when no fluorspar is present, but when four percent fluorspar is present no spinel is detected above 900°C. Up to about 900°C the fluorspar remains in the clay and is identifiable as such in both clays S and M. Fluorspar is detected only at four percent concentration because less than this cannot be detected by x-rays. By 950°C the fluorspar is no longer detectable but it has produced changes in the detectable crystalline phases that are not observed in the absence of fluorspar until much higher temperatures.

Clay S that contains two percent fluorspar forms some detectable mullite at 950°C, but at four percent fluorspar, mullite is clearly detectable along with some feldspar. It was not possible to determine which feldspar is formed, but it is believed to be anorthite. At 1000°C mullite can be detected at one-half percent fluorspar, and at two percent fluorspar the feldspar phase is also present. At 1100°C mullite is detected for the first time in the untreated clay, but feldspar is not detected until at least two percent fluorspar is present. In general, the free quartz content decreases gradually from 900°C on in clays with and without fluorspar; however, in the clay that contains fluorspar the decrease is much more rapid. Four percent fluorspar at 1100°C causes almost a complete disappearance of the free quartz.

In review, the addition of fluorspar to clay S produces mullite, in amounts detectable by x-ray examination, at temperatures 100° to 150°C lower than that required to produce mullite in the absence of fluorspar. Fluorspar in clay S also produces a feldspar which is not detected at any temperature in the absence of fluorspar. It will also be observed that no cristobalite is observed at any temperature or fluorspar concentration. This is probably due to free quartz being used up in forming glass before it can invert to cristobalite. The very fine particle size of the free quartz would allow it to form glasses readily with the high flux content of the illite and the added fluorspar.

Clay M, containing two percent and four percent fluorspar, shows mullite and cristobalite at 950°C. At 1000°C only one-half percent of fluorspar produces some mullite, and with two percent, cristobalite and feldspar are forming in addition to mullite. Near 1100°C, mullite and cristobalite are de-

Table 9.—The Crystalline Phases Identified in Clays S and M by X-Ray Diffraction

Clay	Fluorspar (percent)	Degrees C							
		800	850	900	950	1000	1100	1200	1300
S	0	I, Q Sl, A	I, Q A, Sl	I, Q A, Sl	I, Q R, A	Q, Sl R, A	Mu, Q	—	Mu, Q
S	½	"	"	"	"	Mu, Q	Mu, Q	—	—
S	1	"	"	"	Q	Mu, Q	Mu, Q	—	—
S	2	"	"	"	Mu, Q	Mu, Q F	Mu, Q F	—	—
S	4	I, Q Sl, Sp. A	I, Q Sl, Sp. A	I, Q Sl, Sp. A	Mu, Q F	Mu, Q F	Mu, Q F	—	—
M	0	I, Q A	—	Q, I A	Q, A R, H	Q, H	Q, Mu C, H	Q, Mu C, H	Q, Mu C
M	½	"	—	"	"	Q, Mu	Q, Mu C, R H	Q, Mu C	—
M	1	"	—	"	Q, Mu A, R H	Q, Mu	Q, Mu C, F R, A H	Q, Mu C, F	—
M	2	"	—	"	Q, Mu C, F H	Q, Mu C, F R	Q, Mu C, F R, A	Q, Mu C, F	—
M	4	I, Q A, Sp.	—	Q, R A, Sp.	Q, Mu C, F H	Q, Mu C, F R	Q, Mu C, F R, A	Q, Mu C, F	—

Mu = mullite; Q = quartz; C = cristobalite; F = feldspar; R = rutile; A = anatase; H = hematite; I = illite; Sl = spinel; Sp. = fluorspar.

tected for the first time in the absence of fluorspar, and with one percent fluorspar content the feldspar phase begins to appear. The effect of fluorspar on clay M is similar to that on clay S. The main difference is that cristobalite is produced from clay M and none is produced by firing clay S under any condition used here. The free quartz content of clay M decreases only a very little up to 1200°C, even with the addition of fluorspar. What decrease takes place is probably due to conversion to cristobalite, since the amount of flux constituent (illite) is low and therefore little glass is formed. Also a hindering factor in the solution of the free quartz in the small amount of glass is the large particle size of most of the free quartz.

In review, it looks as though fluorspar aids the formation and growth of mullite crystals at much lower temperatures than they otherwise would develop, thus permitting mullite to be detected by x-ray diffraction techniques. Without fluorspar, mullite of sufficient crystallinity to be detected by x-rays is produced, but only at a 150°C higher temperature. Feldspar is produced in clays S and M only when heated with fluorspar. It is not known whether the feldspar is formed on heating or crystallizes from a glassy phase on slow
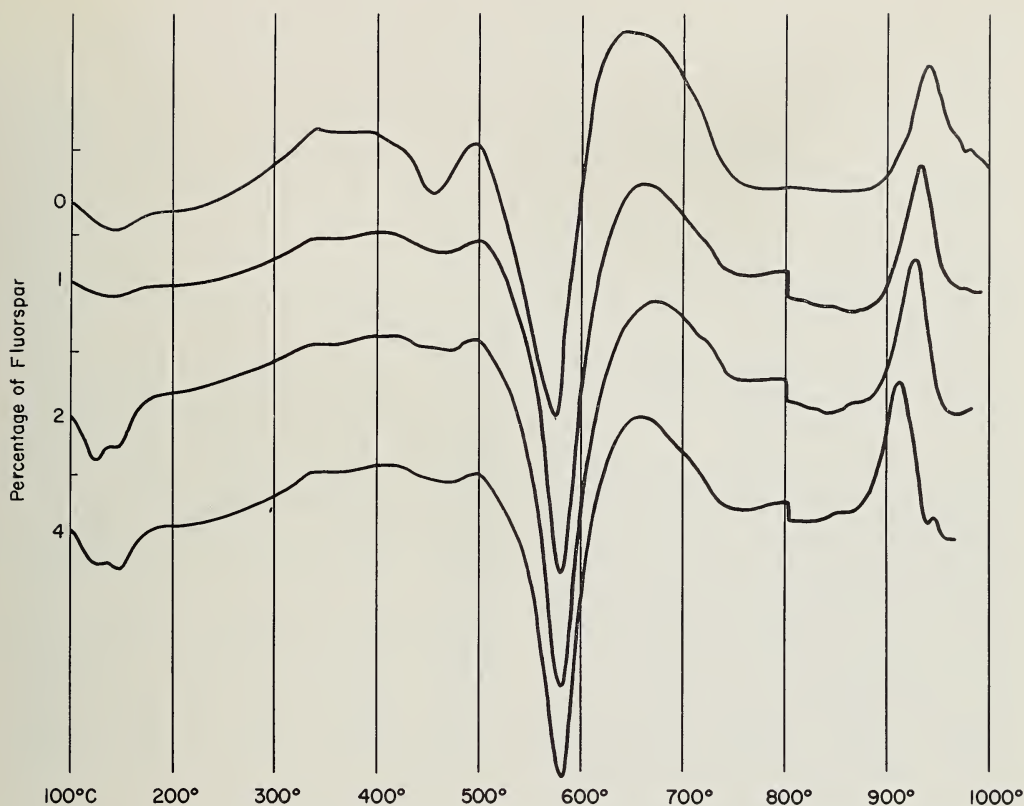
Fɪɢ. 5.—Effect of fluorspar on the D.T.A. diagram of clay S.

cooling. When the free quartz is low and very fine grained, when the illite, which is a flux-carrying material, is high, and the kaolinite content is low, cristobalite is not detected. When the quartz is very coarse, little flux material is present, and the kaolinite content is high, cristobalite is detected for the first time at 1100°C without fluorspar and at 950°C with four percent fluorspar. This cristobalite could be from decomposition of the kaolinite or from inversion of the quartz.

The differential heating curves for clays S and M containing zero, one, two, and four percent fluorspar are shown in figures 5 and 6. The heating rate for both clays was 10°C/min. and in both cases the nickel sample holder was covered with a nickel block. In figure 5, the curve for zero fluorspar was determined at sensitivity 10 (50 microvolts/in.) up to 500°C then switched to scale 20 (100 microvolts/in.) to 600°C then back to scale 10 for the remainder of the diagram. The rest of the curves in figure 5 and all the curves in figure 6 were run on scale 20 to 800°C then on scale 10 to 1000°C.

In figure 5, the presence of the endotherms at 150° and 580°C and the exotherm at 950°C would indicate the presence of only poorly crystalline kaolin and the illite content (known to be present from x-ray analysis) would be missed entirely, as shown by Grim (1947) in his work on mixtures of clay minerals. The small endothermal peak at about 450°C is due to pyrite (Grim
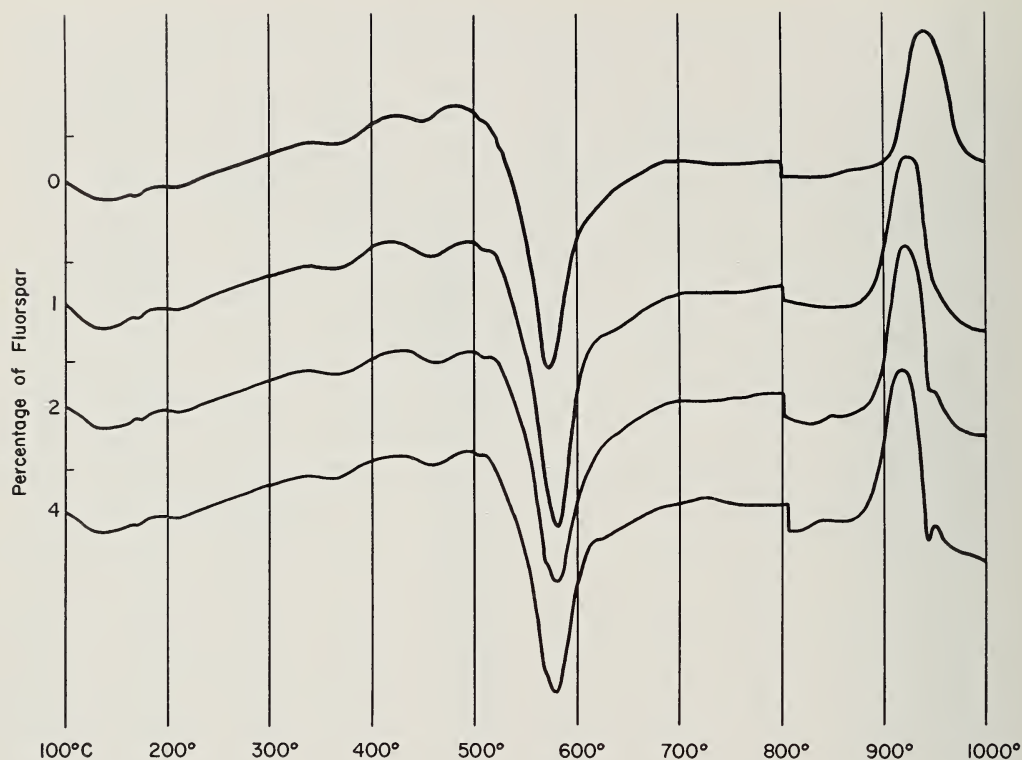
FIG. 6.—Effect of fluorspar on the D.T.A. diagram of clay M.

and Rowland, 1944). This peak is exothermic when the crucible is not covered and there is sufficient oxygen to burn the sulfur as it is released and thus produce heat. It appears that the oxidation of the sulfur (from the decomposition of the pyrite) and the organic matter produces the broad exothermic hump between 600° and 700°C. In short, the restricted oxygen supply pushes the elimination of the sulfur and organic matter to higher temperatures.

Figure 5 shows that the addition of fluorspar has little effect on the shape of the curves up to about 900°C. However the exothermic peak between 900° and 1000°C is sharpened and shifted to lower temperatures, and at four percent fluorspar a new exotherm is noted at 950°C. The alteration of the position and shape of the exothermal peak between 900° and 950°C coincides with the temperature at which fluorspar disappears and mullite and feldspar appear in the x-ray analysis (see table 9). This shift of the exothermal peak is linear for clay S, as shown in figure 7. This indicates that the fluorspar lowers the temperature at which the mullite nuclei first appear. The fact that it can be detected by x-ray analysis as soon as it is formed indicates that fluorspar also influences the growth and perfection of the mullite nuclei. The second faint exothermal peak at 950°C may be associated with perfection of the mullite nuclei or possibly with the formation of the feldspar phase.

These observations agree essentially with the current literature except that
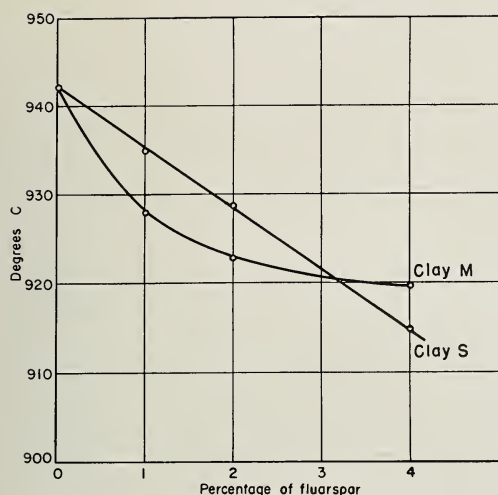
Fig. 7.—Effect of fluorspar content on the major exothermal peak temperature.

the feldspar phase is not reported elsewhere. Palmeri (1951) studied with x-rays and the electron microscope the effect of mineralizers on the mullitization of kaolinite. He found that in the absence of a mineralizer the kaolinite retained its characteristic shape up to 1190°C, but when three percent CaF_2 is added, the particle shape disappears at less than 1000°C and mullite is detected in the x-ray pattern. Nazarenko and Sviridenko (1953) studied the influence of mineralizers on mullite formation from Al_2O_3 and SiO_2 (quartz). They found LiF the most effective mineralizer and CaF_2 only slightly less effective. They showed that the fluorides were more effective than the corresponding carbonates.

The curves in figure 6 are very similar to those in figure 5 except that the exothermal peak between 600° and 700°C has been eliminated. This probably indicates less organic matter in clay M. The peak between 900° and 1000°C is sharpened up slightly and shifted to lower temperatures as for

clay S. However, figure 7 shows that the shift is not linear as it was for clay S. A second small exothermal peak in clay M appears at about 950°C when the fluorspar content is two percent or more. The reason for the appearance of this second small exotherm at 950°C may be the same as given for clay S, that is, it could be associated with the mullite and/or feldspar development.

INFLUENCE OF FLUORSPAR ON THE FIRED PROPERTIES OF "PURE" CLAY MINERALS

Clays S and M contain mixtures of the clay minerals illite and kaolinite, so in an attempt to get a clearer picture of the influence of heat and fluorspar on these minerals, more or less pure samples of each were investigated with two and four percent fluorspar additions. The x-ray patterns were analyzed after firing to various temperatures and the differential heating curves were run. A general discussion of the influence of heat and fluorspar on the clay minerals follows.

The Georgia kaolin was a highly crystalline mineral with about five to ten percent of impurities, which were mainly free quartz, anatase, and illite. The illite sample from Illinois contained no free quartz, but contained some hydrous iron oxides (as goethite) as shown in the D.T.A. diagram (fig. 10) by the endothermic peak between 350° and 400°C (Grim and Rowland, 1942). The kaolin from Anna, Illinois, was of very low crystallinity and contained a large amount (20 to 25 percent) of free quartz. The crystalline phases identified in each fired sample are summarized in table 10.

On heating the Georgia kaolin that contained no fluorspar, the only new crystalline phases up to 950°C are due to impurities. At 1000°C some γ-Al_2O_3

Table 10.—Influence of Fluorspar on the Crystalline Phases Identified in Georgia Kaolin, Anna Kaolin, and Illite

Clay	Fluorspar (percent)	Degrees C				
		900	950	1000	1100	1200
Georgia kaolin	0	I, A	I, A	γ–Al_2O_3 A, Mu	Mu	Mu
"	2	"	"	"	Mu, F, C	Mu, F, C
"	4	A, Sp.	Mu, F	Mu, F	Mu, F, C	Mu, F, C
Anna kaolin	0	Q	Q	Q	Q, Mu	Mu, Q, C
"	4	Q	Mu, Q	Mu, Q, F	Mu, Q, F C	Mu, Q, F C
Illite	0	I, H	Sl, H	Sl, H	Mu, Sl, H	Mu, Sl, H
"	2	"	Mu, Sl, H	"	Sl, H	"
"	4	I, H, Sl Sp.	Mu, Sl, F H	Sl, H, F	"	Sl, H

Mu = mullite; Q = quartz; C = cristobalite; F = feldspar; R = rutile; A = anatase; H = hematite; I = illite; Sl = spinel; Sp. = fluorspar.

and mullite are present and at 1100°C only mullite is detected. When two percent fluorspar is added the same phases are present up to 1000°C, but at 1100° feldspar and cristobalite are detected, in addition to mullite. At four percent fluorspar the unreacted CaF_2 was detected at 900°C, but at 950°C only mullite and feldspar were detected and by 1100°C cristobalite has also appeared. It should also be noted that no visual evidence of vitrification was apparent in any of these samples.

The Anna kaolin shows no detectable mullite until 1100°C and at 1200°C cristobalite also is detected. At four percent fluorspar mullite is detected at 950°C; at 1000°C feldspar and mullite are present and at 1200°C, mullite, feldspar, and cristobalite are detected. The free quartz content remains the same to 1100°C when no fluorspar is present, then decreases slightly at 1200°C. However, when fluorspar is present the free quartz decreases gradually from 1000°C on, and at 1200°C it is less than half the original content.

It should be noted that Anna kaolin itself became progressively harder to grind as the temperature increased, but when four percent fluorspar was added the difficulty in grinding increased markedly with temperature. This may indicate some vitrification.

X-ray patterns of the illite specimens showed a general lack of crystalline material and in all cases where crystalline phases did develop the amounts were very small. Consequently, the interpretation of the illite patterns given in table 10 is very poor and not considered very reliable. The presence of fluorspar seems to promote mullite and feldspar formation at 950°C to 1000°C; however, by 1100°C to 1200°C neither can be detected. It is possible that the fluorspar has promoted the solution of the feldspar and mullite in the glass at high temperatures.

Figure 8 shows that the only influence of fluorspar on Georgia kaolin is the shifting of the 960°C exothermic peak to slightly lower temperatures.
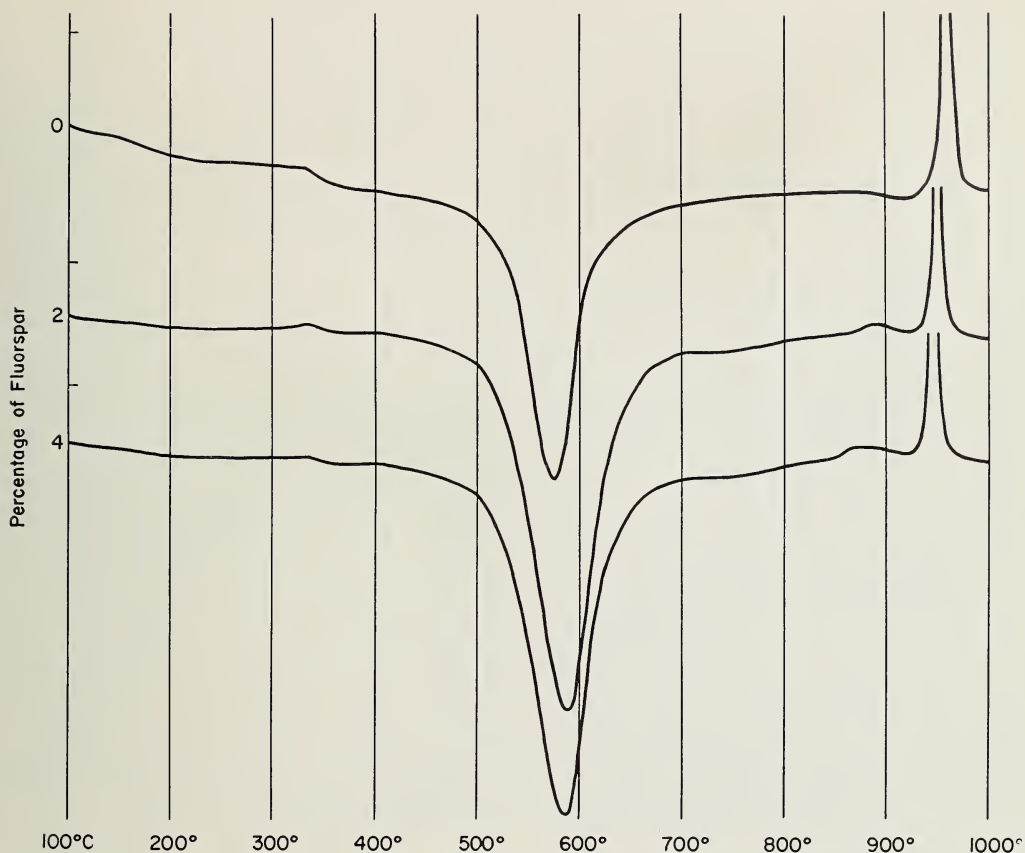
F<small>IG</small>. 8.—Effect of fluorspar on the D.T.A. diagram of Georgia kaolin.

At four percent fluorspar the shift amounts to about 15°C. The thermogram for Anna kaolin (fig. 9) shows a shift of the 940° exothermic peak to about 920°C. A second small exothermic peak between 900° and 1000°C does not appear in either of these clays. So the effect of fluorspar on well crystallized and poorly crystallized kaolins appears to be very similar up to 1000°C in spite of the large amount of free quartz impurity in the Anna kaolin.

In figure 10, at zero percent fluorspar, the only peak not due to illite is the slight endotherm between 350° and 400°C. This has been interpreted as coming from geothite (FeO(OH)) (Grim and Rowland, 1942), an impurity in the clay. On the addition of two percent fluorspar the only difference is a sharpening up of the exotherm at about 920°C. On the addition of four percent fluorspar the intensity of the endotherm at about 900°C and the exotherm at 930°C is much diminished and at 950°C a second small exotherm appears. According to Grim and Rowland (1942), (for illite containing no fluorspar) the first endotherm at about 160°C is due to the loss of adsorbed moisture. The next endotherm, which is associated with the illite, is at about 580°C; this is where most of the lattice water is lost forming the anhydrous modification. From 580°C on, the an-
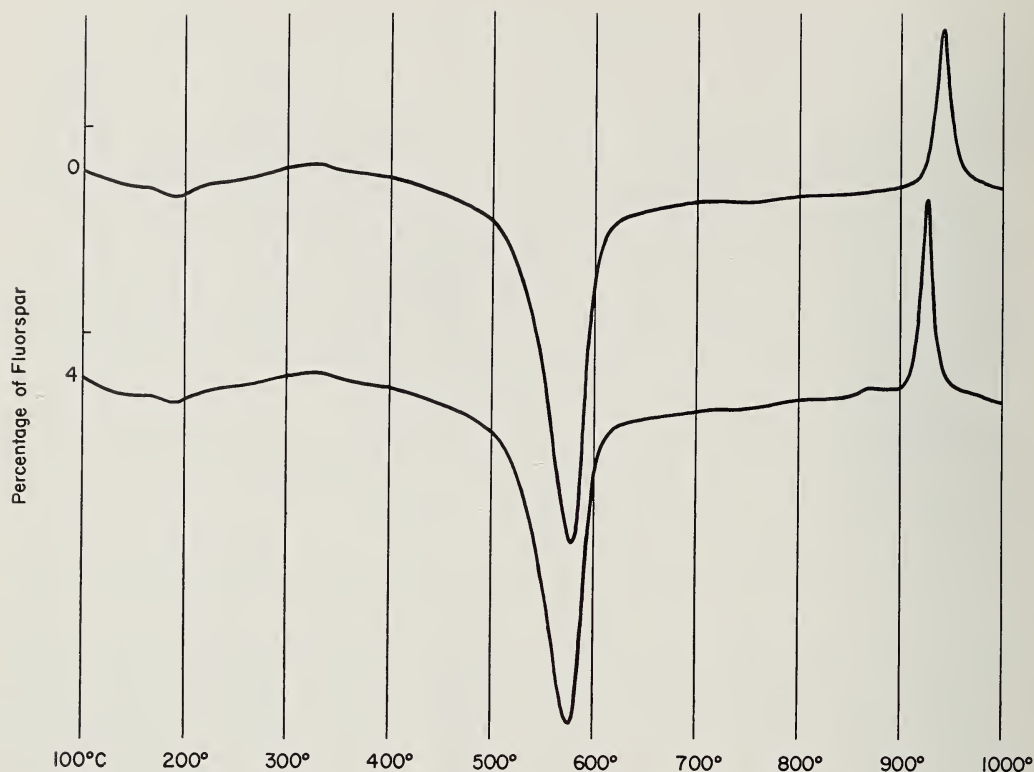
Fig. 9.—Effect of fluorspar on the D.T.A. diagram of Anna, Illinois, kaolin.

hydrous modification of the illite slowly disappears and the endotherm at about 880°C is the point at which the anhydrous modification is destroyed. The exotherm at about 920°C is associated with the formation of the spinel. From this, one may guess that the slight exotherm at 950°C (in the sample containing four percent fluorspar) may well be due to crystallization of mullite or feldspar.

DISCUSSION OF THE EXPERIMENTAL RESULTS

The clays studied here fall into two general categories. Clays S and W are fine-grained and contain about 80 percent clay minerals, which are composed largely of illite. These clays are not highly refractory, as is shown by the fact that water absorption values

fall rapidly above 950°C and that they overfire between 1200° and 1300°C. When fluorspar is present they overfire at lower temperatures. The high illite content is probably responsible for the low refractoriness of these clays.

Clays M and L are coarse-grained and clay M contains only 50 percent clay minerals which are made up largely of kaolinite. The coarse fraction of clay M is mainly quartz. Both of these clays are refractory, as indicated by water absorption values. In clay M this is attributed to the high kaolinite and quartz and low illite content. In fact, clay M is currently being produced and sold as a refractory for low- to moderate-temperature use.

The clays of both categories show very little extractable vanadium after heating up to 650°C. However, after
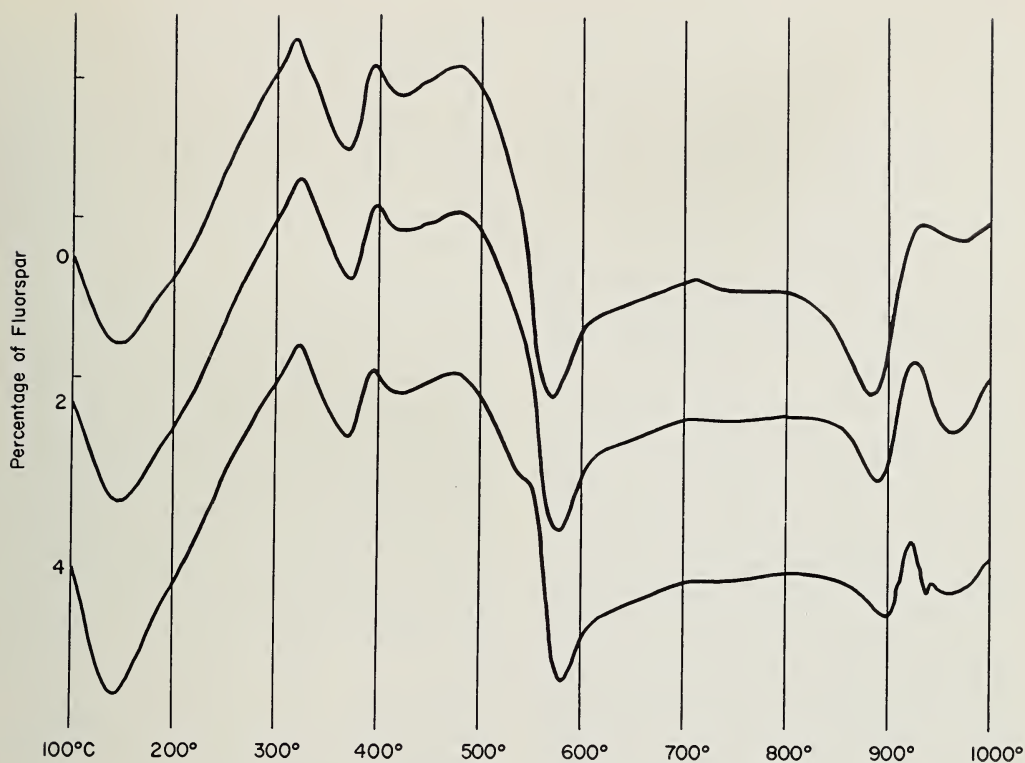
Fig. 10.—Effect of fluorspar on the D.T.A. diagram of illite.

heating above this temperature, the amount of vanadium extracted rises rapidly until a maximum is reached at around 950°C. Heating above this temperature causes the amount of extractable vanadium to fall. However, clays S and W show a more rapid decline than clays M and L. The curves showing water absorption versus firing temperature show this same trend. For clays S and W the water absorption falls very rapidly above 950°C whereas clays M and L show only a gradual decrease in water absorption and even when heated to 1300°C never reach the low values that clays S and W attain. Figures 3 and 4 show these relationships for clays S and M, which are representative members of the two major categories. From this it appears that the amount of vanadium extractable

follows the water absorption curves when no fluorspar is present. When the water absorption curve falls rapidly with rising temperature, the extractability curve also falls rapidly.

The general shape of the curves in figures 3 and 4, when no fluorspar is present is consistent with two successive mechanisms. From 650° to 950°C a reaction is taking place that produces the highly colored, water-soluble vanadium compounds from the insoluble compounds in the raw clay. The water-soluble compounds are believed to be mainly vanadium compounds with Na, K, and Ca. At 950°C this reaction appears to be arrested by the onset of vitrification, and above 950°C the vitreous phase formed from the clay seems to take the water-soluble vanadium compounds into solution, or in

essence make them water-insoluble. If a greater amount of vitreous phase is formed at a given temperature above 950°C, more of the soluble vanadium compounds will be dissolved in this vitreous phase and hence the extractability curve will fall more rapidly.

If this is correlated with the clay mineral compositions of the clays, one sees that clay S, with the highest illite content, shows the most rapid decrease in the amount of extractable vanadium. It is known that illite begins to vitrify (Grim and Rowland, 1942) near 950°C, the peak extractability temperature, and with rising temperatures produces more vitreous phase with which to take water-soluble vanadates into solution. Clay M, which contains a much smaller proportion of illite, produces much less vitreous phase, hence the decline in the extractability curve is not as rapid. It is of course possible that this may be just fortuitous and that other unsuspected factors may be more important than the type of clay minerals present.

The wick test results correspond very well, visually, with the extraction curves shown in figures 3 and 4. It was noted for clay S (containing no fluorspar) that when a sufficiently high temperature has been reached, where the extractable vanadium has fallen to a level of one to two p.p.m., no colored efflorescence is noted on the bar tips after a seven-day wick test, but for clay M (containing no fluorspar) the extractable vanadium must be less than one p.p.m. to be assured of no colored efflorescence. There are, of course, some exceptions, but these appear to be good figures for the major part of the experimental data. Clay M, containing no fluorspar, must be fired to 1200° to 1300°C to produce a bar with no seven-day efflorescence. For clay

L the corresponding temperature is 1100° to 1200°C and for clays S and W it is 1000° to 1100°C. When four percent fluorspar is present clay S shows no seven-day efflorescence after firing to 900° to 950°C but clay M must be fired at 1100° to 1200°C to effectively eliminate colored efflorescence.

It is felt that the rate of decline of the extractability curve, above 950°C, is an important factor in controlling vanadium staining without the addition of fluorspar. The ideal situation would be a sudden drop from the peak to less than one p.p.m. in the temperature range of 950° to 1050°C, the usual firing temperature employed in industrial manufacture. Since this is not the usual case, fluorspar can be added to help control the vanadium efflorescence.

Figures 3 and 4 show the influence of fluorspar on clays S and M. The fluorspar greatly reduces the amount of extractable vanadium in both clays S and M. It will be noted for clay S, in figure 3, that with increased fluorspar content the extractability peak was shifted to lower temperatures. This indicates that the arresting reaction has started at lower temperatures. However, the slope of the extraction curve at temperatures above the extractability peak is about the same as it was at zero percent fluorspar.

Clay M shows no shift in the extractability peak to lower temperatures until the concentration of fluorspar reaches four percent. The slope above the peak, that is, on the high temperature side, at all fluorspar concentrations is about the same. Evidently the fluorspar does not change the slope of the curve above the extractability peak, but does cause changes in the properties of the glass phase and vari-

ous other changes which tie up the soluble vanadates at lower temperatures.

The shift in the D.T.A. curves and the x-ray analysis show that adding fluorspar apparently promotes the growth of crystalline phases at lower temperatures. The fact that new phases are developed at lower temperatures probably has no direct connection with vanadium efflorescence. However the breakup of the clay lattice, the variation in the extractable vanadium, and the appearance of new phases all within the same limited temperature range, suggest strongly that these phenomena are in some way interrelated. It is a well established fact that new reactions take place more readily immediately following the break up of existing phases.

Figure 11 shows water absorption versus the vanadium extracted, for all temperatures above the extractability peak shown in figure 3. This shows that at zero percent fluorspar the amount of extractable vanadium follows the water absorption. However, when fluorspar is introduced the amount of extractable vanadium falls rapidly, although the water absorption remains constant for a considerable period at temperatures of 800° to 950°C. This would seem to indicate that the amount of extractable vanadium is greatly decreased without increasing the amount of glassy phase (lowering of the water absorption). So from this it looks as though the fluorspar must be influencing the properties of the vitreous phase already present. Recent work by Yee, Machin, and Andrews (1955) has shown that fluorspar decreases the viscosity of enamel glasses. Three percent of fluorspar reduced the viscosity 50 percent at 900°C. This suggests that the fluorspar may be re-
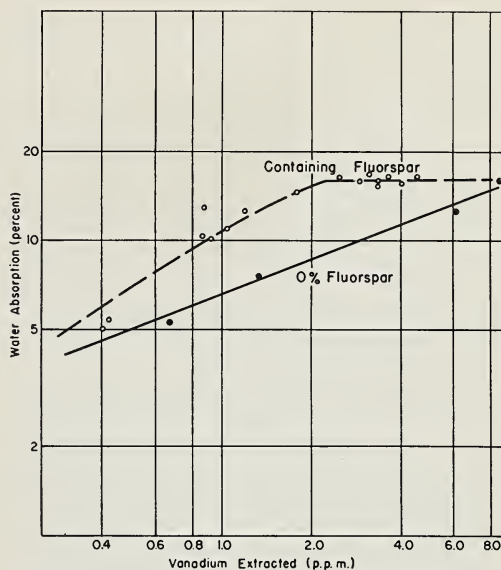

Fig. 11.—Relationship between water absorption and extracted vanadium for clay S.

ducing the viscosity of the vitreous phase formed in the clays so that it can diffuse more readily through the structure and dissolve more of the vanadium-containing compounds, thus tying up the vanadium so that it cannot be water-extracted. At the same time, this more fluid liquid may be catalyzing the formation and growth of new phases at lower temperatures. The water absorption, after the constant interval, drops rather rapidly, beginning at temperatures of 950°C or higher, indicating that additional glass is forming, which lowers the water absorption of the bar and further decreases the amount of extractable vanadium.

Whatever the true mechanism may be, it is important to notice that *low* concentrations of fluorspar are effective in preventing vanadium efflorescence at *low* firing temperatures only when certain types of clay minerals are present. In short, the clay minerals must in themselves be conducive to vitrification if small concentrations of

fluorspar are to be effective in controlling vanadium efflorescence in the usual commercial firing range.

Another important fact to be noted is that all the firing operations in the present study were carried out in an electric furnace with a clean, oxidizing atmosphere. The influence of combustion gases in commercial coal or gas-fired kilns might substantially change the results reported here.

SUMMARY AND CONCLUSIONS

Fluorspar has an inhibiting effect on the tendency of brick made from buff-firing clays to develop vanadium stain. This effect is much more pronounced in cases where the clays are of low refractory character, that is, where a considerable proportion of the clay minerals present are illitic. For clays in which the clay minerals are predominantly kaolinitic and the quartz content is high, the effect of fluorspar is small and requires higher temperatures and more fluorspar for its development. The most probable mechanism for this inhibiting effect is believed to be solution of the vanadium compounds in glass that begins to form as vitrification is initiated in the brick.

The vanadium is essentially in a water-insoluble form in all of the four raw clays tested. It was more concentrated in the fine fractions, which include most of the clay minerals. This of course does not preclude the possibility that vanadium may occur in some finely divided state independent of the clay minerals. The evidence favoring the theory that vanadium is intimately associated with the clay mineral may be summarized as follows:

1) The vanadium is more concentrated in the fine fractions.

2) The greatest amount of water-soluble vanadium appears in the temperature region where breakup of the clay lattice (indicated by x-ray studies and D.T.A. curves) occurs.

3) Hathaway (1955) has presented evidence that vanadium occurs as a substituent for aluminum in the lattice of clay-like silicates containing vanadium.

Vanadium remains relatively water-insoluble in clays which have been heated to temperatures below 700°C. As the heating temperature is carried higher, progressively more of the vanadium becomes water-soluble until about 950°C is reached when the amount of water-soluble vanadium begins to fall off rather rapidly (more rapidly for illite-bearing clays).

Analyses of the colored materials on the tips of wick test bars indicate that colored efflorescence contains principally vanadium as the colorant with smaller amounts of molybdenum. Sodium, potassium, calcium and magnesium are present in amounts proportionately greater than vanadium. Sulfate is present in considerable quantity. The relative abundance of calcium and the alkalies as compared to vanadium leads one to suspect that in many cases where there appear to be large amounts of colored efflorescence on a brick wall the effect may really be largely due to ordinary white efflorescence which is masked by a strong dyeing action of highly colored vanadium compounds.

No evidence was found to indicate that significant amounts of vanadium are eliminated by volatilization at temperatures likely to be used in firing building brick.

REFERENCES

ASTM, 1955, Standard Method of Test for Water Absorption: A.S.T.M. Standards, Part 3, p. 736-738 (1955).

BERTRAND, D., 1950, The Biogeochemistry of vanadium: Bull. Am. Museum of Nat. Hist., v. 94, art. 7, p. 412.

BOSAZZA, V. L., 1940, Occurrence of vanadium and molybdenum in clays: Nature, v. 146, no. 370, p. 746.

BRITTON, H. T. S., and ROBINSON, R. A., 1930, Physicochemical studies of complex acids, II, vanadic acid: Jour. Chem. Soc., 1930, p. 1261.

CURRY, E. R., 1926, Notes on green scumming: Jour. Am. Ceram. Soc., v. 9, p. 392.

FIOLETOV, A., 1929, Investigation of some rare constituents of clays: Keram. Rundschau, v. 37, p. 659.

GRIM, R. E., 1947, 1948, Differential thermal curves of prepared mixtures of clay minerals: Am. Mineralogist, v. 32, no. 9 and 10, p. 493; Illinois Geol. Survey Rept. Inv. 134, p. 11.

GRIM, R. E., and BRADLEY, W. F., 1940, Investigations of the effect of heat on the clay minerals illite and montmorillonite: Illinois Geol. Survey Rept. Inv. 66; Jour. Am. Ceram. Soc., v. 23, p. 242.

GRIM, R. E., and ROWLAND, R. A., 1942, Differential thermal analysis of clay minerals and other hydrous materials: Am. Mineralogist, v. 27, no. 11, p. 750; Illinois Geol. Survey Rept. Inv. 85.

GRIM, R. E., and ROWLAND, R. A., 1944, Differential thermal analysis of clays and shales, a control and prospecting method: Illinois Geol. Survey Rept. Inv. 96, p. 10.

HAMMER, A. J., 1953, You can eliminate green efflorescence: Brick and Clay Record, v. 123, no. 3, p. 37.

HAMMER, A. J., 1955, Occurrence of vanadium in clays, I: Ceram. Age, v. 65, no. 4, p. 47.

HAMMER, A. J., 1955, Occurrence of vanadium in clays, VI: Ceram. Age, v. 66, no. 4, p. 28.

HATHAWAY, J. C., 1955, X-ray diffractometer studies of some vanadium silicates, trace elements investigation: U. S. Geol. Survey Rept. TEI 542.

HECHT, H., and CRAMER, E., 1902, The collected writings of Herman August Seger, v. I, p. 381: The Chemical Publishing Co., Easton, Pa.

JAHR, K. F., and JANDER, G., 1934, Polyvanadates which crystallize from potassium vanadate solutions of different hydrogen-ion concentration: Z. anorg. allgem. Chem., v. 220, p. 201.

JANDER, G., and JAHR, K. F., 1933, Building-up and breaking-down of higher molecular inorganic compounds in solution, for example, vanadium acids, polyvanadates and vanadium salts: Z. anorg. allgem. Chem., v. 212, p. 1.

KALLAUNER, O., and HRUDA, O., 1922, The occurrence of vanadium ceramic raw materials and products and its effect on the fusibility as well as the color and formation of efflorescence in pure kaolin and a typical brick clay: Sprechsaal, v. 55, no. 30, p. 333; no. 31, p. 345.

KALLAUNER, O., and KOKTA, J., 1941, Vanadium efflorescence: Stavivo, v. 22, p. 189.

LEUTWEIN, F., 1941, Geochemie und Vorkommen des Vanadiums: Ber. freiberger geol. Ges., v. 18, p. 73.

LOVEJOY, E., 1934, Classification of fluorescence: Bull. Am. Ceram. Soc., v. 13, no. 1, p. 22.

NAZARENKO, M. F., and SVIRIDENKO, V. A., 1953, Mineralizing effect of some additions on the mullitization process: Vestnik Akad. Nauk. Kazakh., S.S.R., v. 10, no. 11, p. 85.

PALMER, L. A., 1929, Vanadium and molybdenum compounds in clays: Jour. Am. Ceram. Soc., v. 12, p. 37.

PALMERI, V. R., 1951, Mullite formation by decomposition of kaolinite: Anales Soc. Cient. Argentina, v. 152, 127.

PRANDTL, W., and MAUTZ, H., 1911, Action of calcium fluoride on vanadium pentaoxide: Ber., v. 44, p. 2582.

SANDELL, E. B., 1950, Colorimetric determination of traces of metals, second ed., p. 613: Interscience Publishers, Inc., N. Y.

YEE, T. B., MACHIN, J. S., and ANDREWS, A. I., 1955, Relation of composition to viscosity of enamel glasses: Jour. Am. Ceram. Soc., v. 38, p. 378.

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